## VII. "On the Refractivities of Air, Oxygen, Nitrogen, Argon, Hydrogen, and Helium." By Professor WILLIAM RAMSAY, Ph.D., LL.D., Sc.D., F.R.S., and MORRIS W. TRAVERS, B.Sc.

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## "On the Densities of Carbonic Oxide, Carbonic Anhydride, and Nitrous Oxide." By LORD RAYLEIGH, F.R.S. Received October 12,—Read December 9, 1897.

The observations here recorded were carried out by the method and with the apparatus described in a former paper,* to which reference must be made for details. It must suffice to say that the globe containing the gas to be weighed was filled at 0° C., and to a pressure determined by a manometric gauge. This pressure, nearly atmospheric, is slightly variable with temperature on account of the expansion of the mercury and iron involved. The actually observed weights are corrected so as to correspond with a temperature of 15° C. of the gauge, as well as for the errors in the platinum and brass weights employed. In the present, as well as in the former, experiments I have been ably assisted by Mr. George Gordon.

### *Carbonic Oxide.*

This gas was prepared by three methods. In the first method a flask, sealed to the rest of the apparatus, was charged with 80 grams recrystallised ferrocyanide of potassium and 360 c.c. strong sulphuric acid. The generation of gas could be started by the application of heat, and with care it could be checked and finally stopped by the removal of the flame with subsequent application, if necessary, of wet cotton wool to the exterior of the flask. In this way one charge could be utilised with great advantage for several fillings. On leaving the flask the gas was passed through a bubbler containing potash solution (convenient as allowing the rate of production to be more easily estimated) and thence through tubes charged with fragments of potash and phosphoric anhydride, all connected by sealing. When possible, the weight of the globe *full* was compared with the mean of the preceding and following weights *empty*. Four experiments were made with results agreeing to within a few tenths of a milligram.

In the second set of experiments the flask was charged with 100 grams of oxalic acid and 500 c.c. strong sulphuric acid. To absorb the large quantity of $CO_2$ simultaneously evolved a plentiful

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* "On the Densities of the Principal Gases," 'Roy. Soc. Proc.,' vol. 53, p. 134, 1893.

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supply of alkali was required. A wash-bottle and a long nearly horizontal tube contained strong alkaline solution, and these were followed by the tubes containing solid potash and phosphoric anhydride as before.

For the experiments of the third set *oxalic* acid was replaced by *formic*, which is more convenient as not entailing the absorption of large volumes of $CO_2$. In this case the charge consisted of 50 grams formate of soda, 300 c.c. strong sulphuric acid, and 150 c.c. distilled water. The water is necessary in order to prevent action in the cold, and the amount requires to be somewhat carefully adjusted. As purifiers, the long horizontal bubbler was retained and the tubes charged with solid potash and phosphoric anhydride. In this set there were four concordant experiments. The immediate results stand thus:—

Carbonic Oxide.

| | |
|---|---|
| From ferrocyanide .......... | 2·29843 |
| ,, oxalic acid ............ | 2·29852 |
| ,, formate of soda ........ | 2·29854 |
| Mean............ | 2·29850 |

This corresponds to the number 2·62704 for oxygen,[*] and is subject to a correction (additive) of 0·00056 for the diminution of the external volume of the globe when exhausted.

The ratio of the densities of carbonic oxide and oxygen is thus 2·29906 : 2·62760; so that if the density of oxygen be taken as 32, that of carbonic oxide will be 27·9989. If, as some preliminary experiments by Dr. Scott[†] indicate, equal volumes may be taken as accurately representative of CO and of $O_2$, the atomic weight of carbon will be 11·9989 on the scale of oxygen = 16.

The very close agreement between the weights of carbonic oxide prepared in three different ways is some guarantee against the presence of an impurity of widely differing density. On the other hand, some careful experiments led Mr. T. W. Richards[‡] to the conclusion that carbonic oxide is liable to contain considerable quantities of hydrogen or of hydrocarbons. From 5½ litres of carbonic oxide passed over hot cupric oxide he collected no less than 25 milligrams of water, and the evidence appeared to prove that the hydrogen was really derived from the carbonic oxide. Such a proportion of hydrogen would entail a deficiency in the weight of the globe of about 11 milligrams, and seems improbable in view of the good agreement of the numbers recorded. The presence of so much hydrogen in carbonic oxide is also difficult to reconcile with the well-known experiments of Professor Dixon, who found that prolonged treatment with phosphoric anhydride was required in order to render the mixture of carbonic oxide and oxygen inexplosive. In the presence of relatively large quantities of free hydrogen (or hydrocarbons) why should traces of water vapour be so important?

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[*] "On the Densities of the Principal Gases," 'Roy. Soc. Proc.,' vol. 53, p. 144.

[†] 'Camb. Phil. Proc.,' vol. 9, p. 144, 1896.

[‡] 'Amer. Acad. Proc.,' vol. 18, p. 279, 1891.

In an experiment by Dr. Scott,[*] 4 litres of carbon monoxide gave only 1·3 milligrams to the drying tube after oxidation.

I have myself made several trials of the same sort with gas prepared from formate of soda exactly as for weighing. The results were not so concordant as I had hoped,[†] but the amount of water collected was even less than that given by Dr. Scott. Indeed, I do not regard as proved the presence of hydrogen at all in the gas that I have employed.[‡]

## *Carbonic Anhydride.*

This gas was prepared from hydrochloric acid and marble, and after passing a bubbler charged with a solution of carbonate of soda, was dried by phosphoric anhydride. Previous to use, the acid was caused to boil for some time by the passage of hydrochloric acid vapour from a flask containing another charge of the acid. In a second set of experiments the marble was replaced by a solution of carbonate of soda. There is no appreciable difference between the results obtained in the two ways; and the mean, corrected for the errors of weights and for the shrinkage of the globe when exhausted, is 3·6349, corresponding to 2·6276 for oxygen. The temperature at which the globe was charged was 0° C., and the actual pressure that of the manometric gauge at about 20°, reduction being made to 15° by the use of Boyle's law. From the former paper it appears that the actual height of the mercury column at 15° is 762·511 mm.

## *Nitrous Oxide.*

In preliminary experiments the gas was prepared in the laboratory, at as low a temperature as possible, from nitrate of ammonia, or was drawn from the iron bottles in which it is commercially supplied. The purification was by passage over potash and phosphoric anhydride. Unless special precautions are taken the gas so obtained is ten or more milligrams too light, presumably from admixture with nitrogen. In the case of the commercial supply, a better result is obtained by placing the bottles in an inverted position so as to draw from the *liquid* rather than from the *gaseous* portion.

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[*] 'Chem. Soc. Trans.,' 1897, p. 564.

[†] One obstacle was the difficulty of re-oxidising the copper reduced by carbonic oxide. I have never encountered this difficulty after reduction by hydrogen.

[‡] In Mr. Richards' work the gas in an imperfectly dried condition was treated with hot platinum black. Is it possible that the hydrogen was introduced at this stage?

Higher and more consistent results were arrived at from gas which had been specially treated. In consequence of the high relative solubility of nitrous oxide in water, the gas held in solution after prolonged agitation of the liquid with impure gas from any supply, will contain a much diminished proportion of nitrogen. To carry out this method on the scale required, a large (11-litre) flask was mounted on an apparatus in connection with the lathe so that it could be vigorously shaken. After the dissolved air had been sufficiently expelled by preliminary passage of $N_2O$, the water was cooled to near 0° C. and violently shaken for a considerable time while the gas was passing in large excess. The nitrous oxide thus purified was expelled from solution by heat, and was used to fill the globe in the usual manner.

For comparison with the results so obtained, gas purified in another manner was also examined. A small iron bottle, fully charged with the commercial material, was cooled in salt and ice and allowed somewhat suddenly to blow off half its contents. The residue drawn from the bottle in one or other position was employed for the weighings.

Nitrous Oxide (1896).

| | | |
|---|---|---|
| Aug. 15 | Expelled from water | 3·6359 |
| „ 17 | ........................................ | 3·6354 |
| „ 19 | From residue after blow off, valve downwards | 3·6364 |
| „ 21 | „ „ valve upwards.. | 3·6358 |
| „ 22 | „ „ valve downwards | 3·6360 |
| | Mean........................ | 3·6359 |

The mean value may be taken to represent the corrected weight of the gas which fills the globe at 0° C. and at the pressure of the gauge (at 15°), corresponding to 2·6276 for oxygen.

One of the objects which I had in view in determining the density of nitrous oxide was to obtain, if it were possible, evidence as to the atomic weight of nitrogen. It may be remembered that observations upon the density of pure nitrogen, as distinguished from the atmospheric mixture containing argon which, until recently, had been confounded with pure nitrogen, led* to the conclusion that the densities of oxygen and nitrogen were as 16 : 14·003, thus suggesting that the atomic weight of nitrogen might really be 14 in place of 14·05, as generally received. The chemical evidence upon which the latter number rests is very indirect, and it appeared that a direct comparison of the weight of nitrous oxide and of its contained nitrogen might be of value. A suitable vessel would be filled, under known conditions, with the nitrous oxide, which would then be submitted to the action of a spiral of copper or iron wire rendered incandescent by an electric current. When all the oxygen was removed, the residual nitrogen would be measured, from which the ratio of equivalents could readily be deduced. The fact that the residual nitrogen would possess nearly the same volume as the nitrous oxide from which it was derived would present certain experimental advantages. If indeed the atomic weights were really as 14 : 16, the ratio ($x$) of volumes, after and before operations, would be given by

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* Rayleigh and Ramsay, 'Phil. Trans.,' vol. 186, p. 190, 1895.

$$\frac{2{\cdot}2996 \times x}{3{\cdot}6359 - 2{\cdot}2996 \times x} = \frac{14}{8},$$

whence

$$x = \frac{7 \times 3{\cdot}6359}{11 \times 2{\cdot}2996} = 1{\cdot}0061,$$

3·6359 and 2·2996 being the relative weights of nitrous oxide and of nitrogen which (at 0° C. and at the pressure of the gauge) occupy the same volume. The integral numbers for the atomic weights would thus correspond to an expansion, after chemical reduction, of about one-half per cent.

But in practical operation the method lost most of its apparent simplicity. It was found that copper became unmanageable at a temperature sufficiently high for the purpose, and recourse was had to iron. Coils of iron suitably prepared and supported could be adequately heated by the current from a dynamo without twisting hopelessly out of shape; but the use of iron leads to fresh difficulties. The emission of carbonic oxide from the iron heated in vacuum continues for a very long time, and the attempt to get rid of this gas by preliminary treatment had to be abandoned. By final addition of a small quantity of oxygen (obtained by heating some permanganate of potash sealed up in one of the leading tubes) the CO could be oxidised to $CO_2$, and thus, along with any $H_2O$, be absorbed by a lump of potash placed beforehand in the working vessel. To get rid of superfluous oxygen, a coil of incandescent copper had then to be invoked, and thus the apparatus became rather complicated.

It is believed that the difficulties thus far mentioned were overcome, but nevertheless a satisfactory concordance in the final numbers was not attained. In the present position of the question no results are of value which do not discriminate with certainty between 14·05 and 14·00. The obstacle appeared to lie in a tendency of the nitrogen to pass to higher degrees of oxidation. On more than one occasion mercury (which formed the movable boundary of an overflow chamber) was observed to be attacked. Under these circumstances

I do not think it worth while to enter into further detail regarding the experiments in question.

The following summary gives the densities of the various gases relatively to air, all obtained by the same apparatus.* The last figure is of little significance.

| | |
|---|---|
| Air free from $H_2O$ and $CO_2$ | 1·00000 |
| Oxygen | 1·10535 |
| Nitrogen and argon (atmospheric) | 0·97209 |
| Nitrogen | 0·96737 |
| Argon | 1·37752 |
| Carbonic oxide | 0·96716 |
| Carbonic anhydride | 1·52909 |
| Nitrous oxide | 1·52951 |

The value obtained for hydrogen upon the same scale was 0·06960; but the researches of M. Leduc and of Professor Morley appear to show that this number is a little too high.

## "On the Application of Harmonic Analysis to the Dynamical Theory of the Tides. Part II. On the general Integration of Laplace's Dynamical Equations." By S. S. HOUGH, M.A., Fellow of St. John's College, and Isaac Newton Student in the University of Cambridge. Communicated by Professor G. H. DARWIN, F.R.S. Received October 27, —Read December 9, 1897.

(Abstract.)

The former part of this paper deals with solutions of Laplace's differential equations for the tides symmetrical with respect to the axis of rotation. In the present part the restriction of symmetry is no longer imposed, and a general solution is sought, the law of depth of the ocean, however, being limited to the case which will admit of both the interior and exterior surfaces being regarded as spheroids of revolution. It is found that, subject to this limitation, if the solution sought represent a simple harmonic motion of any period whatsoever, and the height of the surface-waves be expressible as an infinite series of tesseral harmonics of the same rank but different orders, a linear relation connecting three successive coefficients of the series can be deduced similar to that obtained in Part I.†

From this relation a period-equation for the free vibrations is deduced, and a method of determining approximate values of the

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* 'Roy. Soc. Proc.,' vol. 53, p. 148, 1893; vol. 55, p. 340, 1894; 'Phil. Trans.,' vol. 186, p. 189, 1895; 'Roy. Soc. Proc.,' vol. 59, p. 201, 1896.

† 'Roy. Soc. Proc.,' vol. 61, p. 236.